

1,2,3,4-Tetra-*O*-acetyl- $\alpha$ -D-glucopyranuronamide

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## Key indicators

Single-crystal X-ray study

$T = 120$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å

$R$  factor = 0.036

w $R$  factor = 0.093

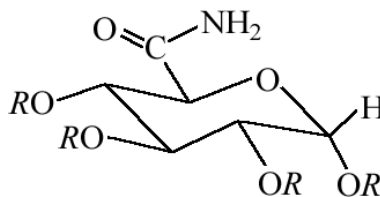
Data-to-parameter ratio = 9.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{14}\text{H}_{19}\text{NO}_{10}$ , forms strong hydrogen bonds *via* amido groups in the [100] direction; soft  $\text{C}-\text{H}\cdots\text{O}$  bonds also act to give chains along both [100] and [001], which combine to form a two-dimensional layer.

## Comment

Extensive intermolecular hydrogen-bonding interactions, involving both the hydroxyl and amido groups, are exhibited in the solid-state structure of  $\alpha$ -D-glucopyranuronamide, (1) (Flippen & Gilardi, 1974): in the monohydrate (1)· $\text{H}_2\text{O}$ , the water molecule additionally takes part in the strong hydrogen bonding linking the molecules (Perrier & Bryn, 1982). As well as the classic, or hard, hydrogen-bonding interactions of hydroxyl and amido groups, *e.g.*  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{O}-\text{H}\cdots\text{O}$ , hydrogen-bonding interactions of a softer nature, such as  $\text{C}-\text{H}\cdots\text{O}$ , are found in (1)· $\text{H}_2\text{O}$ . In general, there is increasing interest in soft hydrogen bonds and their influence on solid-state assemblies (Desiraju, 1991, 1996; Steiner & Desiraju, 1998; Steiner, 1997).



(1)  $R = \text{H}$

(2)  $R = \text{Ac}$

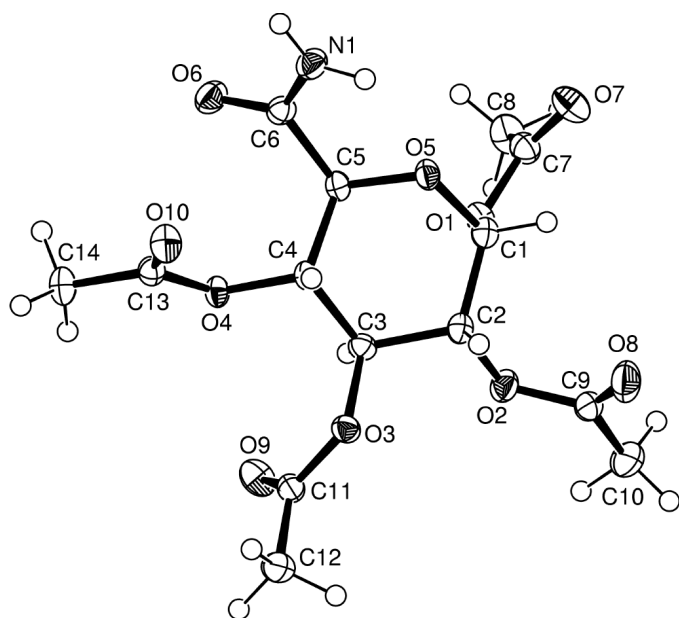
In 1,2,3,4-tetra-*O*-acetyl- $\alpha$ -D-glucopyranuronamide, (2), intermolecular hydrogen bonding falls into two categories: I, strong hydrogen-bonding interactions,  $\text{N1}-\text{H1B}\cdots\text{O6}^i$  [symmetry code: (i)  $x-1/2, -y+5/2, -z$ ], involving just the amido group atoms, and II, a series of soft  $\text{C}-\text{H}\cdots\text{O}$  interactions (Table 2). The strong hydrogen bond results in chains in the [100] direction *via* operation of a  $2_1$  screw axis (Fig. 2).

The soft  $\text{C}-\text{H}\cdots\text{O}$  bonds all involve carbonyl O atoms as acceptors, and either  $\text{H}-\text{C}$  (pyranose ring) or  $\text{CH}_3$  H atoms as donors, resulting in the formation of an overall two-dimensional sheet (Fig. 3). In this compound, the H atoms in the acetyl group are more acidic than those in simple alkanes due to the electron-withdrawing effects of the adjacent carbonyl group, and hence it is valid to consider the  $\text{CH}_3$  groups as H-atom donors. Three soft hydrogen bonds, namely  $\text{C2}-\text{H2}\cdots\text{O9}^{\text{ii}}$ ,  $\text{C8}-\text{H8C}\cdots\text{O7}^{\text{iii}}$  and  $\text{C14}-\text{H14C}\cdots\text{O10}^{\text{iii}}$ , form chains *via* simple translation in the [100] direction (symmetry

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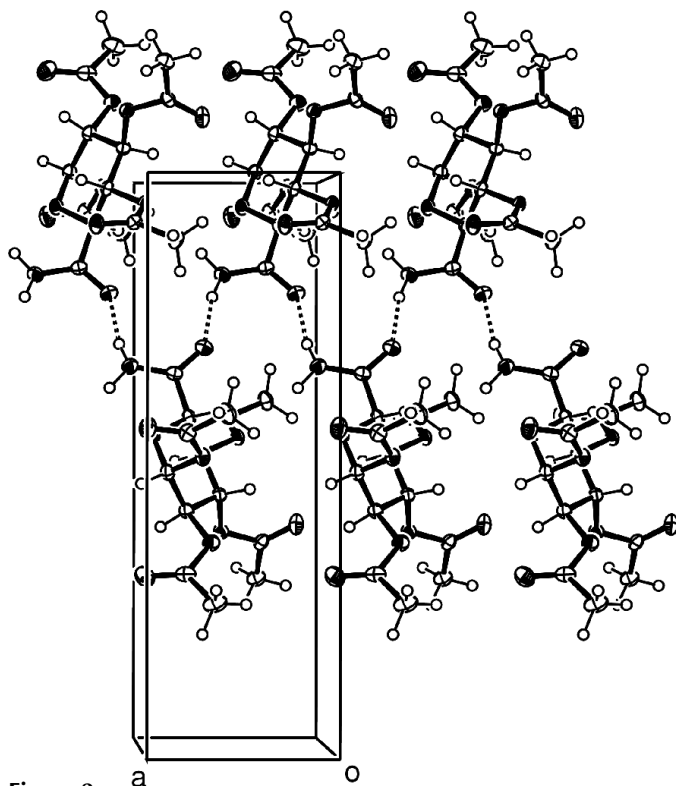
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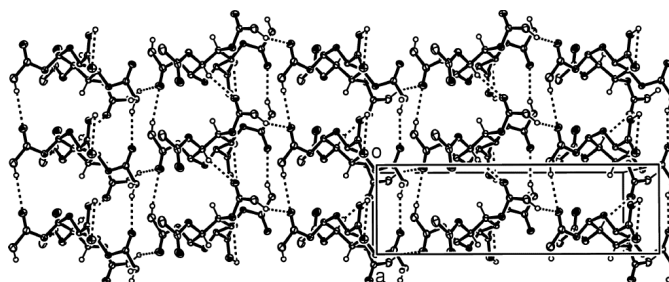


**Figure 1**  
The molecular structure of (2), showing 50% probability ellipsoids.

codes are in Table 2). Another soft hydrogen bond, C14—H14A···O6<sup>v</sup> also forms chains along [100] *via* operation of a  $2_1$  screw axis. Finally, a chain forms from C12—H12C···O7<sup>iv</sup> interactions in the [001] direction, again *via* action of a  $2_1$  screw axis. The intramolecular hydrogen bonds are also listed in Table 2.



**Figure 2**  
Chains formed by the strong hydrogen bond, N1—H1B···O6<sup>i</sup>, in the [100] direction. [Symmetry code: (i)  $x-1/2, -y+5/2, -z$ .]



**Figure 3**  
A two-dimensional sheet formed by soft hydrogen bonds, C2—H2···O9<sup>ii</sup>, C8—H8C···O7<sup>iii</sup> and C14—H14C···O10<sup>iii</sup>, in the [100] and [001] directions, C14—H14A···O6<sup>v</sup> along [100] and C12—H12C···O7<sup>iv</sup> along [001]. [Symmetry codes: (ii)  $x-1, y, z$ ; (iii)  $x+1, y, z$ ; (iv)  $-x+1/2, -y+2, z-1/2$ ; (v)  $x+1/2, y+5/2, -z$ .]

The Cremer and Pople puckering parameters,  $Q = 0.570(2) \text{ \AA}$ ,  $\theta = 13.6(2)^\circ$  and  $\varphi = 307.0(9)^\circ$  (Cremer & Pople, 1975), indicate that the conformation of the pyranose ring in (2) is near  ${}^4C_1$ , with a slight distortion in the direction towards  $E_1$  (Koll *et al.*, 1994).

## Experimental

Acetic anhydride (10 ml) was added to a solution of D-glucopyranuronamide (1.00 g, 5.2 mmol) in pyridine (10 ml). The reaction mixture was stirred overnight and rotary evaporated. The syrupy residue was crystallized from diethyl ether/petroleum ether (40–60), m.p. 418–421 K, literature value 420–422 K (Barton *et al.*, 1994); yield 1.53 g, 82%.  ${}^1\text{H NMR}$  (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.05 (s, 6H, 2Me), 2.08 (s, 3H, Me), 2.20 (s, 3H, Me), 4.30 (*d*, 1H,  $J = 10.1$  Hz, H-5), 5.09 (*dd*, 1H,  $J = 3.7, 10.1$  Hz, H-2), 5.25 (*t*, 1H,  $J = 10$  Hz, H-4), 5.54 (*t*, 1H,  $J = 10.0$  Hz, H-3), 6.26 (*br s*, 1H, NH)\*, 6.38 (*d*, 1H,  $J = 3.7$  Hz, H-1), 6.52 (*br s*, 1H, NH)\*. The two NH signals can appear as a single broad peak in moist  $\text{CDCl}_3$ .  ${}^{13}\text{C NMR}$  (63 MHz,  $\text{CDCl}_3$ ):  $\delta$  20.4, 20.6, 20.8, 68.9, 70.1, 70.3, 88.3, 168.9, 169.3, 169.76, 176.79, 169.9. IR (KBr):  $\nu$  ( $\text{cm}^{-1}$ ) 3480, 3230, 1748, 1668, 1417, 1383, 1220, 1175, 1134, 1041, 943, 563. MS( $\text{ES}^+$ ): 384.1 [100%,  $M + \text{Na}^+$ ], 745.2 [50%,  $2M + \text{Na}$ ]. MS( $\text{ES}^-$ ): 360.2 [100%,  $M - \text{H}^-$ ]. X-ray data were collected by the EPSRC National Crystallography Service at the University of Southampton, England, and MS data were obtained by the EPSRC National Mass Spectrometry Service Centre at the University of Wales, Swansea.

### Crystal data

$\text{C}_{14}\text{H}_{19}\text{NO}_{10}$   
 $M_r = 361.30$   
Orthorhombic,  $P2_12_12_1$   
 $a = 5.5811(2) \text{ \AA}$   
 $b = 16.9550(6) \text{ \AA}$   
 $c = 17.7323(6) \text{ \AA}$   
 $V = 1677.96(10) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.430 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
Cell parameters from 9393 reflections  
 $\theta = 2.9\text{--}27.5^\circ$   
 $\mu = 0.12 \text{ mm}^{-1}$   
 $T = 120(2) \text{ K}$   
Block, colourless  
 $0.25 \times 0.20 \times 0.20 \text{ mm}$

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)  
 $T_{\text{min}} = 0.764, T_{\text{max}} = 0.992$   
10 467 measured reflections

2217 independent reflections  
1926 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.054$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -7 \rightarrow 7$   
 $k = -19 \rightarrow 21$   
 $l = -22 \rightarrow 22$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.036$   
 $wR(F^2) = 0.093$   
 $S = 1.04$   
 2217 reflections  
 238 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0584P)^2 + 0.1398P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

O5—C1	1.410 (2)	C4—O4	1.435 (2)
O5—C5	1.432 (2)	C4—C5	1.534 (3)
C1—O1	1.429 (2)	C5—C6	1.517 (3)
C1—C2	1.530 (3)	C6—O6	1.231 (3)
C2—O2	1.446 (2)	C6—N1	1.332 (3)
C2—C3	1.522 (3)	N1—H1A	0.92 (3)
C3—O3	1.454 (2)	N1—H1B	0.87 (3)
C3—C4	1.519 (3)		
C1—O5—C5	112.31 (16)	C4—C3—C2	111.53 (17)
O5—C1—O1	109.78 (15)	O4—C4—C3	106.92 (16)
O5—C1—C2	110.76 (15)	O4—C4—C5	110.79 (15)
O1—C1—C2	108.65 (17)	C3—C4—C5	108.70 (15)
O2—C2—C3	106.22 (17)	O5—C5—C6	110.20 (17)
O2—C2—C1	110.57 (15)	O5—C5—C4	107.48 (15)
C3—C2—C1	113.58 (17)	C6—C5—C4	112.21 (16)
O3—C3—C4	107.74 (15)	N1—C6—C5	116.85 (19)
O3—C3—C2	105.76 (16)		

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N1—H1B $\cdots$ O6 <sup>i</sup>	0.87 (3)	1.99 (3)	2.840 (3)	165 (3)
C2—H2 $\cdots$ O9 <sup>ii</sup>	1.00	2.29	3.168 (3)	146
C8—H8C $\cdots$ O7 <sup>iii</sup>	0.98	2.55	3.366 (3)	141
C12—H12C $\cdots$ O7 <sup>iv</sup>	0.98	2.60	3.392 (3)	138
C14—H14A $\cdots$ O6 <sup>v</sup>	0.98	2.57	3.529 (3)	166
C14—H14C $\cdots$ O10 <sup>iii</sup>	0.98	2.46	3.283 (3)	142
N1—H1A $\cdots$ O5	0.92 (3)	2.29 (3)	2.658 (2)	103 (2)
C3—H3 $\cdots$ O9	1.00	2.36	2.734 (3)	101
C4—H4 $\cdots$ O10	1.00	2.32	2.682 (2)	100
C5—H5 $\cdots$ O1	1.00	2.36	2.776 (2)	104

Symmetry codes: (i)  $x - \frac{1}{2}, \frac{3}{2} - y, -z$ ; (ii)  $x - 1, y, z$ ; (iii)  $1 + x, y, z$ ; (iv)  $\frac{1}{2} - x, 2 - y, z - \frac{1}{2}$ ; (v)  $\frac{1}{2} + x, \frac{5}{2} - y, -z$ .

It was not possible to determine the absolute configuration of the molecule, and thus the conformation of the precursor sugar was adopted. Friedel pairs were averaged. Most H atoms were placed geometrically and refined using a riding model. The exceptions were H atoms in the amido group (N1), which were located from a difference map and refined freely.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL* (McArdle, 1994, 2000) and *ORTEPIII* for Windows (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2000) and *SHELXL97*.

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## References

- Barton, D. H. R., Gero, S. D., Quicquet-Sire, B. & Samadi, M. (1994). *Tetrahedron Asymmetry*, **5**, 2123–2126.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–37.
- Blessing, R. H. (1997). *J. Appl. Cryst.* **30**, 421–426.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 290–296.
- Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565–565.
- Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
- Flippin, J. L. & Gilardi, R. D. (1974). *Acta Cryst.* **B30**, 537–539.
- Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Koll, P., Saak, W., Pohl, S., Steiner, B. & Koss, M. (1994). *Carbohydr. Res.* **265**, 237–248.
- McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.
- McArdle, P. (2000). *OSCAIL* for Windows. National University of Ireland, Galway, Ireland.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Perrier, P. R. & Bryn, S. R. (1982). *J. Org. Chem.* **47**, 4677–4680.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2000). *PLATON*. May 2000 version. University of Utrecht, The Netherlands.
- Steiner, T. (1997). *Chem. Commun.* pp. 727–734.
- Steiner, T. & Desiraju, G. R. (1998). *Chem Commun.* pp. 891–892.